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Scaling laws for some physical properties of the L_3 (sponge) phase

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Abstract. — The swollen lamellar phase L_α and the anomalous isotropic phase L_3 (sponge) are presently the only two dilute phases of fluid membranes in amphiphilic systems that have been clearly characterized We here deal with the L_3 phase. We first recall the scale invariance argument leading to the ϕ^3 scaling law for the free energy density of phases of fluid membranes We extend it further in order to derive scaling laws for several static and dynamic physical properties of L_3 The effects of renormalizations of the membrane area and of its elastic constants with scale length are discussed. These predictions are checked against a large set of experimental data obtained from light scattering, electric birefringence and flow birefringence The results obtained are puzzling since static quantities exhibit logarithmic corrections due to renormalizations while dynamic ones do not.

Introduction.

The equilibrium state and the physical properties of polymer solutions in the dilute and the semi-dilute regimes are known to be dominated by the statistics of the bending conformations of the long flexible unidimensional molecules Although it is very difficult to work out exactly the corresponding statistical physics, many important insights have been obtained on the basis of simpler scaling arguments [1].

In the recent years, it has become clear that, under suitable experimental conditions, amphiphilic molecules do aggregate in the form of very large flexible 2D-bilayers even in very dilute solutions [2]. Presently, two dilute phases of such fluid flexible membranes have been well characterised in amphiphilic systems : the swollen lamellar phase L_α and the anomalous

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isotropic phase L_3 (sponge phase). The swollen lamellar phase L_α corresponds to the case where the infinite bilayers are regularly stacked parallel to each other so as to determine in the sample a quasi long range smectic order. The L_3 phase is isotropic and shows no long range positional order. Experimental investigations [3-6] involving scattering techniques and measurements of transport properties have suggested the so called bicontinuous topology for the L_3 structure, the membrane being multiconnected to itself throughout the sample as schematized in figure 1.

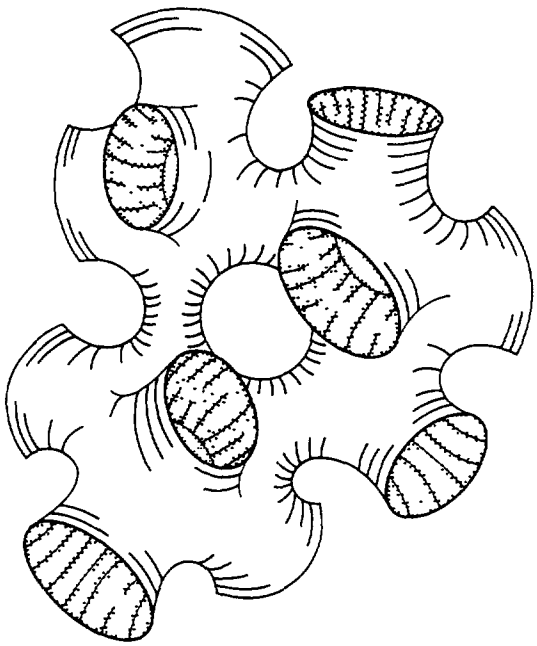

Fig 1 — Schematic drawing of the multiconnected membrane in the L_3 structure

The basic characteristic features of the structure assumed for L_3 are i) the multiconnected membrane separates the 3D space in two **equivalent** [7] subspaces each of them self connected through out the sample ; ii) in spite of the absence of a long range positional order, a characteristic distance $\bar{d}$ clearly appears in the scattering profiles (maximum of $S(q)$) which can be identified as the average size of the « passages » in figure 1. The conservation of total area of membrane A then implies that $\bar{d}$ must scale as ϕ^{-1} where ϕ is the volume fraction of membrane in the sample. At sufficiently high dilution (small ϕ), $\bar{d}$ can so be made very large compared to the thickness δ of the bilayers and also to the range of the repulsive direct molecular interactions. In that limit the bilayer can be assumed to interact through **self avoidance** only. Just like in the case of semi dilute long polymer solutions, we then expect the equilibrium state of L_3 samples to be dominated by the statistics of the bending conformations of the flexible membrane. Here again, although it is not possible to compute explicitly the partition function [8], scaling arguments provide accurate predictions that can be checked against experimental data.

In the first section, we briefly recall how the ϕ^3 dependence of the free energy density of phases of infinite fluid membranes can be derived from a very general stand point. Actually, this scaling law was first derived by Huse and Leibler [8] for the restricted case of swollen

cubic phases (exhibiting long range crystalline order so that the fluctuations of the membranes can be expanded into normal modes). Later on [6], Porte *et al* showed it to be very general, based on a simple scaling argument with no respect to the presence or absence (like in L_3) of long range order It therefore applies to all cases where infinite fluid membranes interacts through self avoidance only.

In section 2, the argument is further extended in order to derive scaling laws for other measurable physical characteristics of the L_3 phase We first recall [6, 7] how the ϕ dependence of the osmotic compressibility is immediately obtained from that of the free energy density. And we present how the argument can be also applied to the collective diffusion coefficient, to the electric birefringence (amplitude and relaxation time) and to the flow birefringence.

In section 3, we discuss the effect of renormalizations of the rigidity moduli K and $\bar{K}$ due to short wavelength curvature fluctuations of the membranes. Following the views first reported in [7], we show that they should induce logarithmic deviations to the scaling laws derived in the frame of exact scale invariance

In section 4, these predictions are compared to experimental results obtained in light scattering (static and quasi elastic), time resolved electric birefringence and flow birefringence.

The static quantities actually exhibit the logarithmic deviations due to renormalization but the dynamic ones do not. This puzzling point is emphasized in the discussion of section 5.

1. Free energy density.

Each accessible bent conformation for the membrane subjected to the only restriction of self avoidance must be weighted by the Boltzmann factor related to the elastic energy to be paid upon bending. The most general expression for the bending energy density of fluid film has been worked out by Helfrich [9] In the particular case of membranes symmetrical with respect to side interchange (symmetrical bilayer) the spontaneous curvature must be zero, and the bending Hamiltonian is

$$H = \int_A \left[\frac{1}{2} K(c_1 + c_2)^2 + \bar{K} c_1 c_2 \right] \mathrm{d}A \tag{1}$$

where c_1 and c_2 are the two principle curvatures of the area element $\mathrm{d}A$. K and $\bar{K}$ are the rigidity moduli respectively associated with the mean curvature $(c_1 + c_2)$ and the Gaussian curvature $(c_1 c_2)$ of the membrane

Scaling laws are often the result of the invariance of some characteristic quantity with respect to a set of spatial transformation. In the present case, the invariant quantity is the elastic Hamiltonian [1] and the spatial transformation is the set of isotropic dilations (i.e. same change in scale in the 3 directions of space) · a dilation of ratio λ will transform $\mathrm{d}A$ into $\lambda^2 \mathrm{d}A$ and each c_1 and c_2 into c_1/λ and c_2/λ so that H remains identical

Let us consider two systems [6] (Fig. 2) consisting of respective total area of membrane A and $A' = \lambda^2 A$ confined in respective volumes V and $V' = \lambda^3 V$ Note that, in the case of the L_3 structure drawn on figure 1, the ratio V/A (respectively V'/A') can be essentially identified with the characteristic distance $\bar{d}(\bar{d}')$ up to some geometrical prefactor of order unity. However, the argument is general enough to be applied even in the case of a structure showing no well defined measurable characteristic distance So, we work it out keeping A and V (rather than A and $\bar{d}$) as the parameters defining the considered situation. Apart from short wavelength thermal ripples (wavelength smaller than $\bar{d}$ and $\bar{d}'$), any configuration

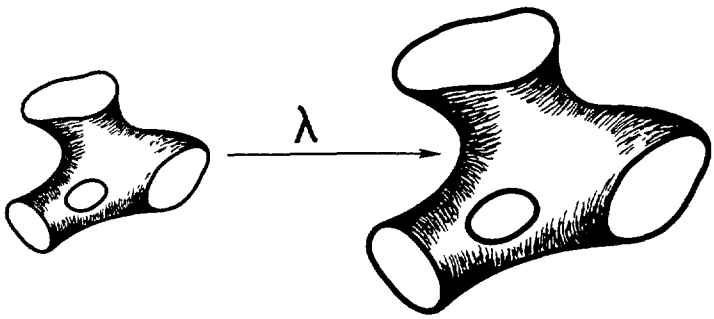

Fig 2 — Dilation transformation applied on a given configuration of the membrane

of the first system corresponds to a « dual » configuration of the second system through the isotropic dilation of ratio λ. Dual configurations having the same elastic energy they have **the same statistical weight** and therefore bring the same contribution to the free energy of each system. This means that, except for the contribution of the ignored small ripples, the **free energy of fluid membranes is also scale invariant just like the elastic energy.** Moreover, it is trivial to show that, in the limit of high K/T values (rigid limit where the high q curvature modes of a flat membrane can be assumed independent), the contribution of the small wavelength thermal ripples is simply proportional to the total area of membrane A (or $A' = \lambda^2 A$). This contribution can therefore be entirely incorporated into the standard chemical potential μ_A per unit area of membrane. Putting together these feature with the extensivity of the free energy, we arrive at the following expression for the free energy of a given sample with area of membrane A confined within the volume V for **a phase consisting of infinite membranes only** [10] (such as L_α and L_3) :

$$F = \mu_A A + B_A(K, \bar{K}, T)\, A^3/V^2 \tag{2}$$

where B_A is an unknown function of K, $\bar{K}$ and T The second term is both extensive and scale invariant. A/V being simply proportional to ϕ ($\phi = \delta A/V$), [2] can be immediately translated in terms of the free energy per unit volume of the sample

$$F/V = \mu_\phi \phi + B_\phi(K, \bar{K}, T) \cdot \phi^3 . \tag{3}$$

The first term, linear in ϕ, is trivial and does not affect the stability and physical properties of the phase. The second term which **scales as** ϕ^3 expresses the scale invariance of the statistics of membranes and plays a central role in the physical properties of the phases : quite a number of other scaling laws can be straightforwardly derived from it as shown in the next section

But before closing the present section, we want to stress again the basic conditions required for the scaling argument to apply. The essential restriction is that the Hamiltonian must be invariant through simple dilation. It therefore apply to the case of membranes interacting through self avoidance only In that respect, the d^{-2} dependence of the effective Helfrich steric interaction [11] in the swollen lamellar phase indeed arises from the scale invariance Further more, the argument also works in the high dilution asymptotic limit when the membranes interact through a net direct **repulsive** potential decreasing with the distance d **faster than** d^{-2} [12] On the other hand, whatever short its range, a net **attractive** interaction obviously breaks the scale invariance of the Hamiltonian : even a sticky potential has an

increasing effect upon dilution (or dilation), presumably leading to a negative ϕ^2 term in the free energy density [13]. Another strong limitation of the approach is the idealisation of the membrane as having only curvature degrees of freedom. In real systems, the possibility of other internal degrees of freedom must be questioned. In particular, in many common surfactant systems, fluid membranes form spontaneously provided that a cosurfactant is used : the additional degree of freedom is the local composition of the membrane, possibly coupled to its local curvature. The contribution of the coupling to the overall Hamiltonian of the system has no reason to be scale invariant and the argument might fail. In the present report, two of the three systems investigated in sections below actually involve membranes made up of mixed surfactant and cosurfactant. Nevertheless, their physical properties are found to agree with the scaling expectations indicating that, for these two systems at least, the composition degree of freedom is not too important.

2. Scaling laws.

2.1 OSMOTIC COMPRESSIBILITY. — Using (3), we immediately derive the osmotic pressure π :

$$\pi = - \left(\frac{F}{V} \right) + \phi \frac{\partial (F/V)}{\partial \phi} \sim \phi^3 . \tag{4}$$

Then, the intensity of light scattered at zero angle ($I(q \to 0)$) being proportional to the osmotic compressibility :

$$I(q \to 0) \sim \phi \left(\frac{\partial \pi}{\partial \phi} \right)^{-1} \tag{5}$$

we expect :

$$I(q \to 0) \sim \phi^{-1} \tag{6}$$

along a dilution line (constant K/T and $\bar{K}/T$).

2.2 KERR CONSTANT. — In an electric birefringence experiment, the sample is submitted to a static electric field **E**. Bilayers being locally anisotropic with uniaxial symmetry oriented along their local normal **n**, they usually exhibit anisotropy of their static dielectric polarizability and therefore a spontaneous tendancy to orient with respect to the electric field. As a result, the initially isotropic structure of L_3 becomes anisotropic under the field and shows measurable optical birefringence Δn :

$$\Delta n = B_K E^2 \lambda_0 \quad (\lambda_0 \text{ wavelength of light}) \tag{7}$$

where the proportionality constant B_K is the so called Kerr constant. Our purpose is here to derive the scaling law for B_K Let us introduce β the average structural anisotropy induced by the electric field We need it to be expressed as a dimensionless quantity, a convenient choice is

$$\beta = \frac{d_{\parallel E} - d_{\perp E}}{d_{\parallel E} + d_{\perp E}} \tag{8}$$

where $\bar{d}_{\perp E}$ and $\bar{d}_{\parallel E}$ are the « unit cell » dimensions along directions respectively normal and parallel to the electric field **E**.

For weak deformations ($\beta \ll 1$) we make a Taylor expansion of the free energy around $\beta = 0$:

$$F(\beta = 0) = [\mu\phi + B(\beta = 0) \cdot \phi^3] \cdot V \tag{9}$$

$$\Rightarrow \Delta F(\beta) = F(\beta) - F(0) = \frac{1}{2}\beta^2 \cdot B''(0) \cdot \phi^3 \cdot V \tag{10}$$

where

$$B''(0) = \left.\frac{\partial^2 B}{\partial \beta^2}\right|_{\beta=0}. \tag{11}$$

The contribution of the electric field to the total energy of the membrane is :

$$-\frac{\Delta\varepsilon}{2} \cdot E^2 \cdot \beta \cdot \delta \cdot A \tag{12}$$

where $\Delta\varepsilon$ is the anisotropy of dielectric constant (at zero frequency) of the membrane, A is the total area of membrane in the volume V. Minimizing the sum of (10) and (12) gives the equilibrium value of β :

$$\beta \sim \frac{1}{2} \cdot \frac{\Delta\varepsilon \cdot E^2 \cdot A}{B''(0) \cdot \phi^3 \cdot V} \sim \phi^{-2} \cdot E^2. \tag{13}$$

Assuming that the resulting optical birefringence Δn only arises from the intrinsic molecular anisotropy of the bilayer we expect

$$\Delta n \sim \phi \cdot B \sim \phi^{-1} \cdot E^2. \tag{14}$$

So finally, the Kerr constant B_K should scale as :

$$B_K \sim \phi^{-1} \tag{15}$$

More generally, we expect all static susceptibilities to scale like ϕ^{-1} in L_3.

2.3 RELAXATION TIMES. — After having suddenly switched off the electric field, the structure will progressively relax back to its isotropic initial state ($\beta = 0$). The rate of free energy variation during that process is :

$$\dot{\Delta F}\left(\beta, \frac{\partial\beta}{\partial t}\right) = B''(0) \cdot \beta \cdot \frac{\partial\beta}{\partial t} \cdot \phi^3 \cdot V. \tag{16}$$

Assuming that all dissipation is due to viscous flows of the solvent inside the « cells » and the « passages », we write for the rate of entropy production :

$$T \cdot \dot{\Delta S} = \frac{1}{2}\eta_0 \int_V \left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i}\right)^2 dV \tag{17}$$

where η_0 is the viscosity of the solvent and v is the velocity field in the solvent At fixed deformation rate $\partial\beta/\partial t$, the velocities at corresponding points in a dilation transformation are indeed proportional to the dilation ratio, but the velocity gradients have the dimension of an inverse time and remain invariant. On the other hand the velocity gradients are indeed proportional to the deformation rate $\partial\beta/\partial t$. We therefore expect $T \cdot \dot{\Delta S}$ to be of the form :

$$T \cdot \dot{\Delta S} \sim \eta_0 \cdot V \cdot \left(\frac{\partial\beta}{\partial t}\right)^2 \tag{18}$$

independent of the dilution ϕ. For sufficiently short times, the relaxation process is adiabatic and no work is exchanged with the outside :

$$\Delta \dot{U} = 0 = \Delta \dot{F} + T \Delta \dot{S} \tag{19}$$

Since $\Delta \dot{F}$ is proportional to ϕ^3 and $T \Delta \dot{S}$ is independent of ϕ we immediately obtain that all relaxation times must scale as :

$$\tau_R \sim \phi^{-3} \tag{20}$$

2.4 DIFFUSION COEFFICIENT. — Indeed similar arguments apply to the dynamics of the relaxation of concentration fluctuations as measured in a quasi elastic light scattering experiment. But the total amount of membrane in the sample is a conserved quantity which means that the relaxation time τ_D must depend on the wave vector q at which it is measured. Assuming simple diffusion we expect :

$$\tau_D^{-1}(q, \phi) = D_c(\phi)\, q^2 \tag{21}$$

where $D_c(\phi)$ is the cooperative diffusion coefficient.

Using the same analysis as before (but keeping in mind that a dilation transformation of ratio λ changes the wave vector q into $q' = q/\lambda$) we simply obtain :

$$\tau_D(q, \phi) = \tau_0(q/\phi) \,.\, \phi^3 . \tag{22}$$

Combining (21) and (22) gives [14] :

$$D_c(\phi) \sim \phi \tag{23}$$

2.5 FLOW BIREFRINGENCE. — A characteristic feature of the L_3 phase is that it shows strong flow birefringence upon gentle stirring We guess indeed that it arises from the coupling between the induced structural anisometry β and the elongational part of the shear stress. In the low shear rate limit (linear regime) we expect the induced anisometry β to lie in the plane of both the velocity and the velocity gradient, tilted at $\pi/4$ off the direction of the velocity gradient The corresponding induced optical birefringence being of the form :

$$\Delta n = B_{\text{flow}}\, \gamma \sim \phi \,.\, \beta \tag{24}$$

where we assume again that the local dielectric constant anisotropy (at optical frequency) only arises from the intrinsic molecular anisotropy of the bilayer. However, B_{flow} cannot be considered as a susceptibility since it is measured in conditions such that energy is steadily injected into the structure by the imposed shear rate γ. It is in a steady dissipative state, out of equilibrium and B_{flow} must be considered as a dynamical characteristic. The induced anisometry β is related to the finite time τ_R necessary for the structure to relax the shear deformation and we expect accordingly :

$$\beta \sim \tau_R \,.\, \gamma \tag{25}$$

where the prefactor is of order unity Keeping in mind that τ_R scales as ϕ^{-3} (see above) and combining (24) and (25) we immediately obtain :

$$B_{\text{flow}} \sim \phi^{-2} . \tag{26}$$

The ϕ dependences predicted in this section are reported in table I.

Table I. — *Scaling laws for the physical properties of the* L_3 *phase.*

Physical poperty	Scaling behavior
Free energy density	$F/V = \mu_\phi \phi + TB(K/T, \bar{K}/T) \phi^3$
Osmotic compressibility	$I(q \to 0) \sim \phi^{-1}$
Kerr constant	$B_K \sim \phi^{-1}$
Diffusion coefficient	$D_c \sim \phi$
Relaxation time of the Kerr effect	$\tau_R \sim \phi^{-3}$
Flow birefringence	$B_{flow} \sim \phi^{-2}$

3. Renormalizations.

Scaling laws for several quantities characterizing the L_3 phase can so be derived as quite direct consequences of the scale invariance of the elastic energy of fluid membranes. But an important point of our argument is that the small ripples can be analysed as combinations of **independent** normal modes (their contribution to the free energy is then simply proportional to A) which is an approximation valid in the rigid limit only ($K/T \gg 1$). In this limit only can the increase of area compared to its projected value be neglected and the dilution be identified with a pure dilation. Perturbation calculations [15-17] worked out recently, have shown that the effect of small wavelength curvature fluctuations is to **renormalize** the effective values of A, K and $\bar{K}$. Up to the first order in T/K, the following expressions for the renormalized quantities have been obtained [17]:

$$A = A_0 \left[1 + \frac{k_B T}{4 \pi K} \ln \left(\frac{\xi}{a} \right) \right] \tag{27}$$

$$K(\xi) = K_0 - \frac{3 k_B T}{4 \pi} \ln \left(\frac{\xi}{a} \right) \tag{28a}$$

and

$$\bar{K}(\xi) = \bar{K}_0 + \frac{10 k_B T}{12 \pi} \ln \left(\frac{\xi}{a} \right) \tag{28b}$$

where A_0 is the area of the projection of the membrane on its average position, K_0 and $\bar{K}_0$ are the bare values of the rigidity moduli (as measured at very small scale length), a is the short wavelength molecular cut off, and ξ the scale at which those effective values are involved. For L_3, the relevant scale length is indeed the structural characteristic length $\bar{d}$ The main consequence of renormalizations is to **break** up to some extent **the scale invariance of the free energy.** Therefore, the ϕ^3 dependence of the free energy density in [3] should be somewhat affected. However, renormalizations of A, K and $\bar{K}$ are all logarithmic in $\bar{d}$ (i.e. in ϕ) and therefore increase very slowly. So finally, for small values of T/K, we expect for the free energy density a ϕ dependence of the form [7]:

$$(F/V)_{L_3} \sim \phi^3 (1 + c \ln \phi) \tag{29}$$

i.e. a main dependence still in ϕ^3 but with a logarithmic correction, the prefactor c being an unknown function of T/K. Consequently, the other scaling laws derived in the preceding section should be as well affected by corrections logarithmic in ϕ [7].

It must be emphasized at this point that (27) (28a) and (28b) are first order corrections (in powers of T/K) in perturbation theory. They are quantitatively reliable in the semi rigid regime only i.e. for situations where the characteristic distance $\bar{d}$ is much smaller than persistence length ξ_K of the bilayer :

$$\xi_K = a \exp\left(\frac{4\pi K_0}{3 k_B T}\right)$$

where a is a molecular size (presumably of the order of the membrane thickness ~ 20 Å). For two systems investigated below (namely CPCI and AOT — see next section) recent measurements of K_0 [22] (K_0(CPCI) ~ 1 5 $k_B T$ and K_0(AOT) ~ 3 $k_B T$) yield ξ_K values (ξ_K(CPCI) ~ 2 × 10^4 Å and ξ_K(AOT) ~ 6 × 10^6 Å) much larger than $\bar{d}$ at all dilutions so that we expect to remain in the first order perturbation regime all along the dilution line The situation is less clear for the third system (betain, see next section) for which we have no reliable data for K_0. but we have good reasons to guess that its rigidity is somewhat lower so that the semi rigid regime is questionable. This point is discussed further in the next section for the purpose of analysis of the electric birefringence data obtained for this later system.

4. Experiments.

Three different systems have been investigated . the quasi binary system AOT/brine [18], the ternary system *n*-dodecylbetain/pentanol/water (betain system) and the quasi ternary system cetylpyridinium chloride/hexanol/brine (CPCI system).

The AOT system was investigated with light scattering (elastic and quasi elastic) in order to check the scaling predictions for the osmotic compressibility and the cooperative diffusion coefficient D_c. All data are collected using a standard AMTEC goniometer with a Brookhaven digital correlator The scattered intensity is collected for each sample as a function of the wave vector q. For dilute samples, appreciable q-dependences are observed (see e g , Fig. 3) which are very well fitted with the theoretical expression proposed by Roux *et al.* in reference [7] :

$$I(q) = A\left[B + \frac{\mathrm{tg}^{-1}(q\xi_{I/O}/2)}{q\xi_{I/O}/2}\right] \tag{30}$$

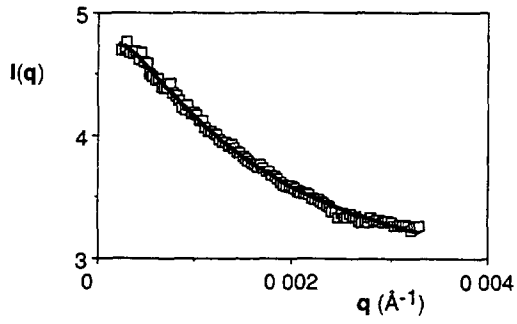

Fig. 3. — q-dependence of the light scattered intensity for the AOT sample with ϕ = 0 487 The full line correspond to the best fit using relation [30] as proposed in [7]

where the correlation length $\xi_{I/O}$ is that of the thermal fluctuations beyond the average I/O (inside/outside) symmetry. From those fits, accurate values of $I(q \to O)$ can be determined for each dilution ϕ In order to exhibit possible logarithmic deviations beyond the expected main ϕ^{-1} dependence for $I(q \to O)$, we have plotted in figure 4 $[\phi . I(O)]^{-1}$ *versus* $\ln \phi$. A straight line is obtained showing that the osmotic compressibility is of the form [7] :

$$I(q \to O) \sim \left[\phi \cdot \ln \frac{\phi}{\phi_I^*} \right]^{-1} \tag{31}$$

consistently with the scaling approach corrected by the renormalizations

For all samples the relaxation of concentration fluctuations as measured by quasi elastic light scattering is a single exponential with a characteristic time τ_D proportional to q^2 (simple diffusion process see Fig. 5) [23] from which a cooperative diffusion coefficient $D_c(\phi)$ can be defined

$$\tau_D^{-1}(q, \phi) = D_c(\phi) . q^2 \tag{32}$$

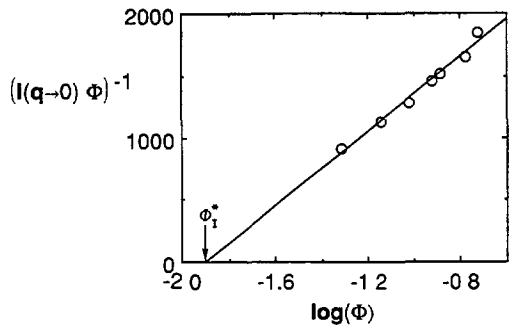

Fig 4

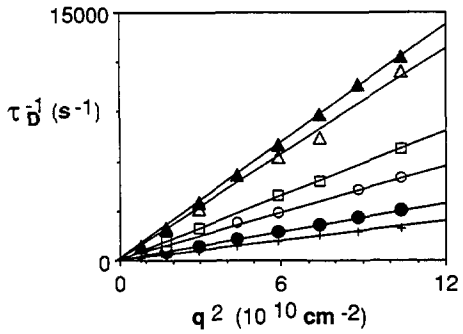

Fig 5

Fig 4 — $[\phi I(O)]^{-1}$ *versus* $\ln \phi$ for the L_3 phase of the AOT system

Fig. 5 — q dependence of the inverse relaxation time τ_D^{-1} for several L_3 samples in the AOT system. Different samples with volume fractions ranging from $\phi = 0\,0487$ and $\phi = 0\,397$

The variations of $D_c(\phi)$ *versus* ϕ are plotted in figure 6. The observed evolution is simply linear :

$$D_c(\phi) \sim \phi \tag{33}$$

the intriguing point being that no logarithmic deviation is observable for that dynamic characteristic quantity (in contrast with the conjugate susceptibility — i.e. the osmotic compressibility) An interesting point is that the order of magnitude for D_c is similar to that of disc like objects of average size $\bar{d}$ (see Tab. II).

Electric birefringence measurements are performed on the L_3 phase of the betain system [19]. For that system the membrane is uncharged at pH 7 and the solvent is pure deionized water and therefore **non conducting.** The samples can thus be submitted to an electric field in

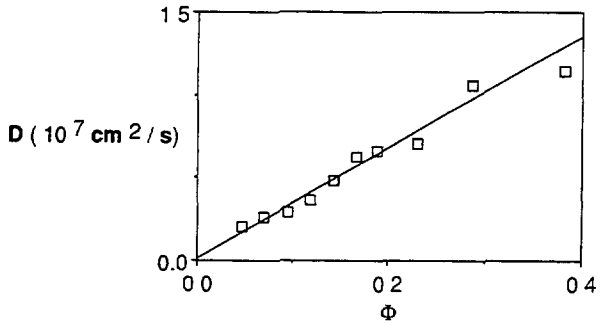

Fig 6 — Evolution of D_c *versus* ϕ for the AOT system

Table II. — *Quasi elastic light scattering data for the* AOT *system.* $\bar{d}$ *are from neutron scattering data reported in* reference [15] *The hydrodynamic length* ξ_H *is derived from* D_c *using the classical relation* $D_c = k_B T/6 \pi \eta_0 \xi_H$ *where* η_0 *is the viscosity of brine. Note that* ξ_H *is of the order of* $\bar{d}$ *at all dilution.*

ϕ	$\bar{d}$ (Å)	D_c (10^{-7} cm^2 s^{-1})	ξ_H (Å)
0 0479	605	0 205	1 200
0 0704	412	0 259	940
0.0952	305	0.294	830
0.119	243	0.368	663
0.143	203	0.477	511
0.167	174	0 627	389
0.188	154	0.661	369
0.230	126	0 706	346
0 287	101	1 06	230
0.383	76	1.14	216

the range $400 < E < 1\,700$ V/cm with no important charge transport. For all investigated samples, the induced optical birefringence is linear in E^2:

$$\Delta n \sim E^2 \tag{34}$$

Which means that we are in the linear regime where the induced structural anisometry β is small : $\beta \ll 1$. Time resolved analysis of the Δn evolution has shown that the rise time of Δn upon switching on the field and the decay time after switching off are identical (Fig. 7)

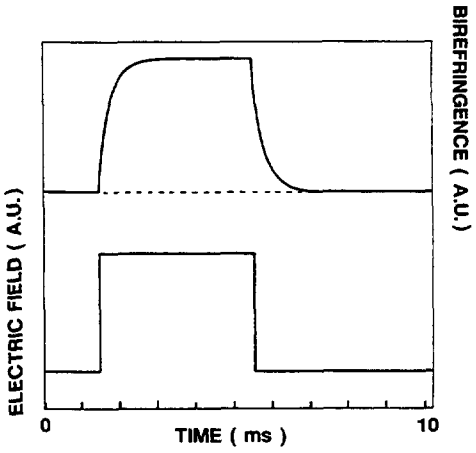

Fig. 7 — Dynamic of the electric birefringence signal for the betain sample with $\phi = 0.0552$ showing that the rise time and the decay time are identical

indicating that there is no permanent dipole effect (purely induced dipole effect). This is further checked making an abrupt reversal of the electric field ($\mathbf{E} \rightarrow -\mathbf{E}$) : nothing noticeable happens on the birefringence signal. The Kerr constant $B_K(\phi)$ can thus be defined safely and measured accordingly, the obtained data being plotted in figure 8 (see also Tab. III) : the Kerr constant is negative at high ϕ, comes to zero around $\phi = 0.07$ and becomes positive at low ϕ's. That change in sign upon dilution is specially intriguing, since it seems to suggest that the structural anisotropy induced by the field has opposite sign depending on the concentration i.e. that the dielectric anisotropy of the membrane is ϕ dependent. This unrealistic possibility can be discarded from observations in polarized light of monocristalline oriented smectic samples of the swollen lamellar phase L_α of the same system. Their optical birefringence also changes sign at essentially the same volume fraction $\phi_0 \approx 0.07$, indicating therefore that this is a purely optical effect for both L_α and L_3 phases. We interpret it according to the explanation proposed by Barois and Nallet [20]. Two contributions to the optical birefringence of the samples have to be considered : the first one is indeed related to the molecular anisotropy of the membrane (this is what we have assumed in the scaling approach of B_K in the preceding section) ; and the second would be present even in absence of any molecular anisotropy of the membrane and arises from the partitioning of space into

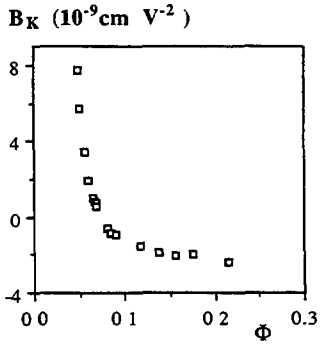

Fig. 8 — B_K *versus* ϕ for the L_3 phase in the betain system

Table III. — *Electric birefringence data for the betain system. $\bar{d}$ is estimated from neutron scattering data obtained for the L_α phase. ξ_H is derived from τ_R using the classical relation $\tau_R^{-1} = 6 k_B T/8 \pi \eta \xi_H^3$. We here only report data far enough from ϕ_0 where τ_R is unambigously defined by a single exponential fit of the relaxation.*

ϕ	τ_R (μs)	ξ_H (Å)	$\bar{d}$ (Å)	B_K (19^{-9} V^{-2} cm)
0.0483	467	800	1 100	7.72
0.0501	416	770		5.69
0.0552	298	690		3.44
0.0603	274	670	770	1.91
0.0654	208	611		1 02
0.137	16.4	262		– 1 92
0.156	10.4	225		– 2.05
0.175	6.87	196		– 2.00
0.215	4.89	175	180	– 2.36

alternate slices of different optical dielectric constants (membrane and solvent). That second contribution being usually called the **form birefringence.** The resulting total anisotropy $\Delta\varepsilon$ of dielectric constant (at optical frequency) has been calculated by Barois and it has the form [20] :

$$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} = \frac{-\phi(1-\phi)(\varepsilon_S - \varepsilon_{M\parallel})(\varepsilon_S - \varepsilon_{M\perp}) + \phi\varepsilon_S(\varepsilon_{M\parallel} - \varepsilon_{M\perp})}{\phi\varepsilon_S + (1-\phi)\varepsilon_{M\parallel}} \tag{35}$$

where the subscript // and ⊥ stand for the directions respectively parallel and normal to the director of the lamellar sample, ε_S is the dielectric constant of the solvent and $\varepsilon_{M\parallel}$ and $\varepsilon_{M\perp}$ are the dielectric constants of the membrane relative to the direction of the director of the sample. The first term in the numerator of [35] corresponds to the form contribution and the second term to the intrinsic contribution In general we expect the form contribution to be negative ($\varepsilon_S < \varepsilon_{M\parallel}$ and $\varepsilon_{M\perp}$) and the intrinsic contribution to be positive and a change in sign is observed at finite ϕ. Finally, the optical birefringence $\Delta n_{L\alpha}$ of a lamellar sample should vary as

$$\Delta n_{L\alpha} = -A\phi + B\phi^2 \tag{36}$$

(A and $B > 0$ are unknown specific constants) at small ϕ.

Anf for a L_3 sample with finite field induced structural anisometry β :

$$\Delta n_{L_3}(\beta) = (-A\phi + B\phi^2)\beta \tag{37}$$

instead of (14) and the scaling law for B_K (15) must be modified in the form :

$$B_K \sim \frac{a_K}{\phi} - b_K \quad (a_K \text{ and } b_K > 0) \tag{38}$$

assuming reasonably that the bilayers preferentially align parallel to the electric field **E** (in order to minimize the depolarization field : $\beta < 0$).

The prediction (38) is checked against the experimental data in figure 9 where B_K is plotted as function of ϕ^{-1} We clearly see a strong upward deviation beyond the linear expectation. Just like in the case of $I(q \to O)$, we wonder whether this deviation is consistent with the logarithmic correction due to renormalizations. If this is so, the field induced anisometry should rather have the form :

$$\beta \sim \left[\phi^2 \cdot \ln \frac{\phi}{\phi_K^*}\right]^{-1} \cdot E^2 \tag{39}$$

instead of (13) and using (37) we finally rather get :

$$B_K \sim \left[\phi \cdot \ln \frac{\phi}{\phi_K^*}\right]^{-1} (a_K - b_K \phi) \tag{40}$$

which gives a relation of the form :

$$\frac{\phi_0 - \phi}{\phi \,.\, B_K} \sim \ln\left(\frac{\phi}{\phi_K^*}\right) \tag{41}$$

where ϕ_0 is the concentration where intrinsic and form birefringences compensate. We check this expectation in figure 10. The expected linear behavior is actually observed which means that the effective scaling law for B_K indeed **involves the logarithmic correction due to renormalization.**

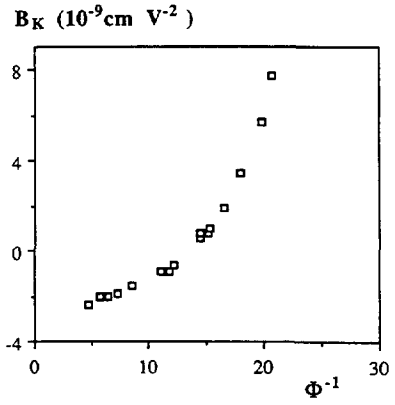

Fig. 9

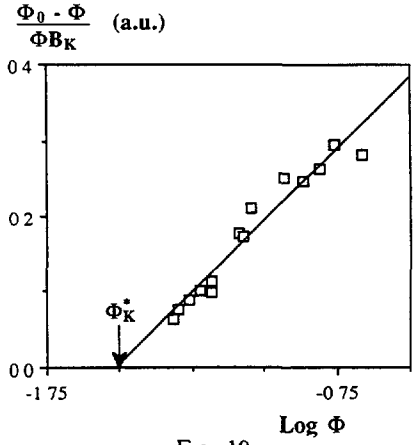

Fig 10

Fig 9 — B_K *versus* ϕ^{-1} for the L_3 phase of the betain system

Fig 10 — $\dfrac{\phi_0 - \phi}{\phi \,.\, B_K}$ *versus* $\ln \phi$ for the L_3 phase of the betain system.

However, although the plot of figure 10 seems convincing, one should wonder whether the most dilute samples (with larger $\bar{d}$) are not too far from the perturbation regime This possibility is actually suggested by the slight downward curvature of the experimental evolution, the lower points (where the experimental accuracy is best) being somewhat below the average straight line. We may consider this behavior as an indication of the onset of higher orders (in T/K) corrections beyond first order

On the other hand, for most samples, the relaxation of the induced birefringence after switching off the field appears very close to a single exponential. In figure 11, we have plotted this relaxation *versus* time in the double logarithmic representation appropriate for investigating plausible stretched exponential behavior. The evolution is actually linear with a slope (0.94) very close to 1. Similar behaviors are observed for all samples with concentrations far enough from the compensation point (ϕ_0). The behavior is farther from a simple exponential for the samples closer to ϕ_0 but we guess that this is related to the fact that the signal is low so that other minor contributions to the birefringence become visible having different dynamics (local molecular reorientation for instance...). So finally in most cases the Kerr relaxation time is well defined and its variations as function of ϕ^{-3} are plotted in figure 12 in order to check its scaling law ($\tau_R \sim \phi^{-3}$) We actually observe the expected linear behavior. In particular the points corresponding to the lower volume fractions are also very well aligned along the ϕ^{-3} scaling indicating no detectable slowing down of the relaxation process at low ϕ So, here again the dynamic quantity shows no logarithmic deviations beyond the mean field scaling law, while the corresponding susceptibility (B_K) clearly does.

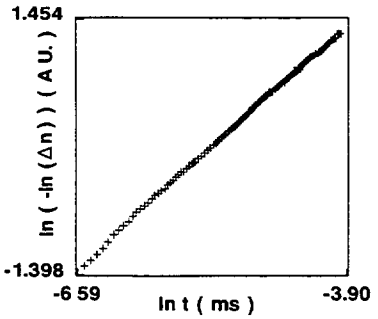

Fig. 11. — ln (− ln (Δn)) *versus* ln t for the L_3 sample with $\phi = 0\,215$ in the betain system.

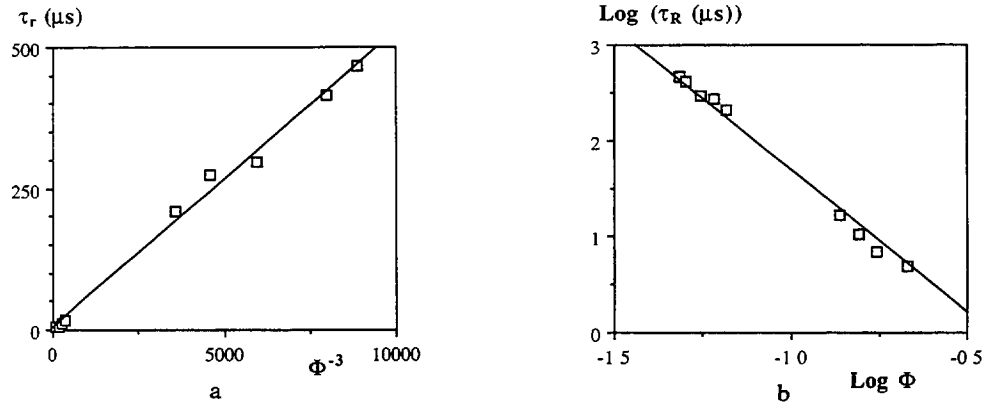

Fig. 12 — a) τ_R *versus* ϕ^{-3} for the betain system b) same data as in 12 a) using logarithmic plot. The full line correspond to the slope 3.

The samples investigated in flow birefringence are from the system CPCI/hexanol/brine which we formerly characterized extensively using mainly neutron scattering technique (see Ref. [3]). The geometry of the flow birefringence experiment is that of a classical Couette cell with outer rotating cylinder, the light beam propagating through the sheared sample along the direction perpendicular to both the velocity and the velocity gradient. The gap between the cylinders is 0.7 mm. And the optical path through the cell is 7 cm long so that the sensitivity of the experiment is very good The observed induced uniaxial birefringence is in all cases found to have its axis titled $\pi/4$ off the direction of the velocity gradient as expected for the linear regime (low shear range). The variations of the phase difference $\Delta\theta$ between the ordinary and the extraordinary light *versus* the shear rate γ are plotted in figure 13 for samples of various concentrations. For all sample $\Delta\theta$ is indeed proportional to γ on the entire investigated shear rate range. Here again we observe a change in sign of the induced birefringence which we also interpret in terms of intrinsic birefringence and form birefringence. For the CPCI system, the compensation concentration ϕ_0 is 0.18, confirmed by optical observation of the swollen lamellar phase L_α. The sign of the induced birefringence (Tab. IV) positive at low ϕ, indicates that the membrane preferentially aligns along the direction of the elongational part of the shear stress as expected indeed. Due to this effect, we have to modify the expected $B_{flow} \sim \phi^{-2}$ scaling law (derived for the case of intrinsic birefringence only) which rather becomes of the form :

$$B_{flow} \sim A\phi^{-2} + B\phi^{-1} \tag{42}$$

To check that, we have plotted in figure 14, $\phi^2 B_{flow}$ *versus* ϕ. The expected linear behavior gives reasonably good agreement with the experimental data (although not excellent). Here again, the scaling behavior of this dynamical quantity shows no clear evidence of any logarithmic deviation related to renormalizations

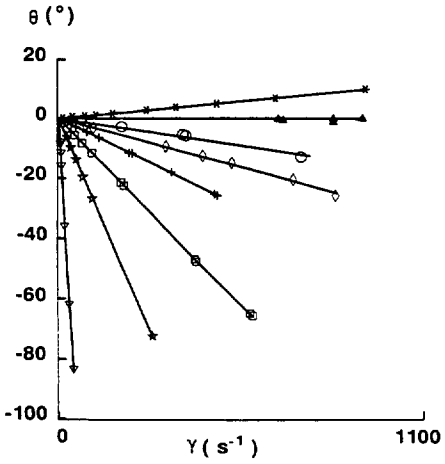

Fig 13

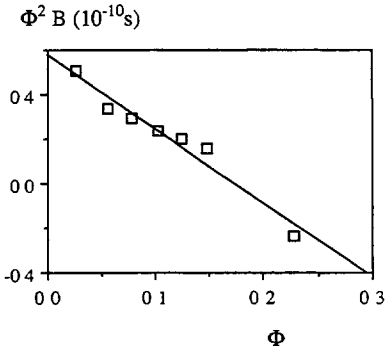

Fig 14

Fig 13 — The phase difference between ordinary and extraordinary light *versus* the shear rate γ in the flow birefringence experiment on the L_3 phase of the CPCI system Several samples ranging from $\phi = 0\,0213$ to $\phi = 0\,225$

Fig. 14 — $\phi^2 B_{flow}$ *versus* ϕ for the CPCI system

Tableau IV. — *Flow birefringence data for the* CPCI *system.*

ϕ	B_{flow} (10^{-10} s)
0.0265	719
0.0561	106
0.0794	46.6
0 102	22 2
0.126	12 4
0.149	6 9
0.228	– 4.48

5. Discussion.

The main purpose of this experimental study was to check the validity of the scaling approach based on the scale invariance of the elastic energy of fluid membranes. We have found that the main dependences are indeed what is expected from the scaling approach for the two static susceptibilities and for the three dynamic properties However, static and dynamic properties behave differently with respect to the marginal logarithmic deviations related to renormalizations of the area and of the rigidity moduli of the membranes. For the two static quantities, the expected logarithmic corrections have to be introduced in order to obtain good quantitative fits. On the other hand, for the three dynamic quantities no deviations from simple scaling behavior could be detected. This difference is actually not a matter of experimental accuracy. Although varying slowly with ϕ, the expected logarithmic deviations correspond to marginal slowing down diverging at finite ϕ value (ϕ^*) instead of $\phi = 0$ as predicted from the mean field approach Such an effect should be specially easy to evidence on the variations of relaxation times which scan more than two orders of magnitudes over the investigated ϕ range. The puzzling difference in behavior between static and dynamic quantities is therefore a real experimental fact. But at the present time, we have no interpretation for it.

One point needs to be underlined : for each static susceptibility, the observed logarithmic corrections involve a particular value ϕ^* for the volume fraction (see Figs. 4 and 10) However ϕ^* must not be identified to the concentration at which the measured susceptibility actually diverges (i.e. « critical volume fraction »). It only arises from the first order correction in T/K beyond the mean field behavior which diverges at $\phi = 0$. Before reaching ϕ^*, higher order terms will also increase and eventually dominate leading to an effective divergence at a different concentration. Even more, since ϕ^* corresponds to a first order correction only, it has no particular reason to be the same for two different susceptibilities measured for the same given system along the same dilution line.

Otherwise, the measured values of D_c for the AOT system and of τ_R for the betain system happen to be quite close to what is expected for an assembly of disc like objects of lateral extension of order $\bar{d}$ (see ξ_H in Tabs. II and III) Similar results have been obtained by Miller

et al. [21] for a different system, and they argued of that as an indication of L_3 being an assembly of discrete discs rather than consisting of a multiconnected membrane. Both models indeed lead to the same scaling laws provided that the diameter of the discs is slaved to be of the order of their separation distance at all dilutions as they propose. Moreover, the prefactors should be also very similar provided that, in the connected model, the K rigidity of the bilayer is of the order of $k_B T$ as is indeed the case for the present systems (we have estimated $K \sim 3\, k_B T$ for the AOT system and $K \sim 0.5\, k_B T$ for the betain system). So, clearly, it is very difficult to discriminate between these two models since they both involve one only characteristic distance $\bar{d}$. However, we underlined in section 4 that the electric birefringence relaxation is remarkably well fitted by a single exponential. In the discrete disks model, this would suggest a very monodisperse population which seems unrealistic for a reversible self assembling process leading to particles of very large sizes. On the other hand, a single relaxation process seems more plausible in the multiconnected model. Anyway, the only truely discriminating procedure is to probe directly the connectivity of the membrane by measuring transport properties of the amphiphilic molecules that are slaved to diffuse into the bilayer [4].

Another point deserves to be discussed further. Following the point of view of Milner *et al.* in reference [14], we expect two separate time ranges for the dynamics of L_3. Within very short times, the spontaneous thermal fluctuations (light scattering) or the field induced deformations (electric birefringence) correspond to structural changes keeping constant the topology of the structure Within much longer times, the topology may have relaxed leading to a wider set of structural fluctuations or deformations. The characteristic time separating those two ranges is the topological relaxation time τ_h it corresponds to the average life time of one given passage in the L_3 structure. According to [14], the most plausible scenario for the disappearance of one passage involves two steps as described along figure 15a b ·

i) shrinking of the passage with a relaxation time τ_S of the order of the time required for the membrane to move on a distance of about $\bar{d}$ (i.e. $\tau_S \approx \tau_R$)

ii) local fusion of the membranes through an activation barrier E_A. So finally the time τ_h should be ·

$$\tau_h \approx \tau_R \exp\left(\frac{E_A}{k_B T}\right). \tag{43}$$

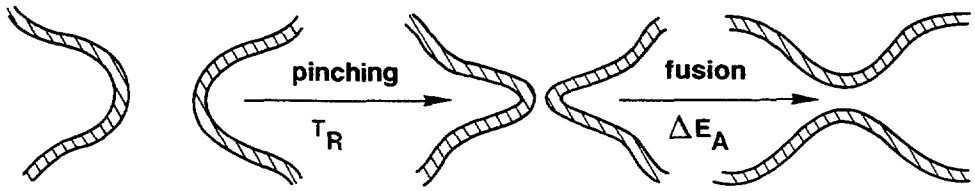

Fig 15 — Plausible mechanism for the spontaneous annihilation of a « passage » [11]

The bilayer being a very stable local structure, we expect E_A to be much larger than $k_B T$ and therefore τ_h should be orders of magnitude larger than τ_R. In that picture we do expect in an electric birefringence experiment two different behaviors depending on the duration t of the electric square pulse. If t is in the range $\tau_R \ll t \ll \tau_h$ the structure is deformed at fixed topology and we basically measure a single relaxation process with the characteristic time τ_R. If on the other hand the pulse duration is very long ($t \gg \tau_h$) then the relaxation

process will involve two successive steps First, the structure deforms at fixed topology in the time τ_R and then deforms further and accomodates a new topological complexity in the time τ_h.

To check that picture, we have submitted the most concentrate sample ($\phi = 0.215$ so that τ_R is very short $\tau_R = 5 \times 10^{-6}$ s) to an electric pulse of long duration ($t \approx 10$ ms). We still obtained a single relaxation response with the characteristic time τ_R. We see only two possibilities to explain that puzzling result. Either the topological time is much larger than 10 ms which implies $E_A \gg 7\, k_B\, T$. Or the anisometry β and the density of topological complexity h (number of handles per unit volume) are not coupled (i.e. $\partial^2 F/\partial\beta\ \partial h \equiv 0$) in the L_3 structure Since there is no particular symmetry reason for the second possibility to be true, we rather guess that E_A is very large. T-jump experiments are presently in progress in order to check that delicate point

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